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OFFICE OF NAVAL RESEARCH

AD-A251 213



Contract N00014-89-J-1041
R&T Code 413C012—04

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JUN 4 1992
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Technical Report No. 18

Reactions of Polymers with Pendant Cyclophosphazenes

by

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Prepared for Publication

in

Polymer Preprints

May 22, 1992

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92-14367

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92 6 01 047

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION		1b. RESTRICTIVE MARKINGS	
2a. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION/AVAILABILITY OF REPORT Available for public release; distribution unlimited	
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE			
4. PERFORMING ORGANIZATION REPORT NUMBER(S) Technical Report No. 18		5. MONITORING ORGANIZATION REPORT NUMBER(S)	
6a. NAME OF PERFORMING ORGANIZATION University of Vermont	6b. OFFICE SYMBOL (if applicable)	7a. NAME OF MONITORING ORGANIZATION ONR	
6c. ADDRESS (City, State, and ZIP Code) Department of Chemistry University of Vermont Burlington, VT 05405-0125		7b. ADDRESS (City, State, and ZIP Code) Office of Naval Research Arlington, VA 22217	
8a. NAME OF FUNDING/SPONSORING ORGANIZATION ONR	8b. OFFICE SYMBOL (if applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER	
8c. ADDRESS (City, State, and ZIP Code) Office of Naval Research 800 North Quincy Arlington, VA 22217		10. SOURCE OF FUNDING NUMBERS	
PROGRAM ELEMENT NO. N00014-89	PROJECT NO. J-1041	TASK NO. 413C012	WORK UNIT ACCESSION NO
11. TITLE (Include Security Classification) Reactions of Polymers with Pendant Cyclophosphazenes			
12. PERSONAL AUTHOR(S) C.W. Allen, K.R. Carter, M. Bahadur and D.E. Brown			
13a. TYPE OF REPORT Reprint	13b. TIME COVERED FROM _____ TO _____	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
16. SUPPLEMENTARY NOTATION Prepared for publication in "Polymer Preprints"			
17. COSATI CODES FIELD GROUP SUB-GROUP		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number) cyclophosphazenes redox polymers polymer reactions	
19. ABSTRACT (Continue on reverse if necessary and identify by block number) The reactions poly(pentachlorovinyloxycyclotriphosphazene), with a variety of amines and oxyanions have been examined. Variable degrees of substitution are obtained and the resulting materials have a complex thermal decomposition process. Copolymers having alkynyl phosphazene side chains react with dicolbalt octacarbonyl to form redox active polymers.			
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION	
22a. NAME OF RESPONSIBLE INDIVIDUAL		22b. TELEPHONE (Include Area Code)	22c. OFFICE SYMBOL

REACTIONS OF
POLYMERS WITH
PENDANT
CYCLOPHOSPHAZENES

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INTRODUCTION

One significant area of interest in the study of hybrid inorganic/organic polymers has been that of chemical reactivity. The ability to effect property modification and/or incorporation of new, useful functionalities via reactions of preformed polymers provides an incentive for pursuit of these studies. The reactions of poly(dichlorophosphazene), $(\text{NPCl}_2)_n$, which have been explored by Allcock and coworkers,¹ are arguably the most extensive for any polymer system. Synthetic transformations of $(\text{NPCl}_2)_n$ with structurally simple units such as fluoroalkoxides gives elastomers with low T_g values while more complex substituents can provide sites for biological or catalytic activity.¹ We have been examining an alternative type of phosphazene polymer in which cyclophosphazenes² are substituents on a linear hydrocarbon chain.² In this paper we report some approaches to applying the wide variety of reactions which have been carried out on cyclophosphazenes to reactions of cyclophosphazenes in a polymeric environment.

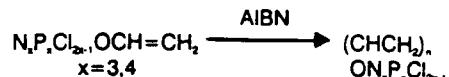
EXPERIMENTAL

Materials. Hexachlorocyclotriphosphazene, $\text{N}_3\text{P}_3\text{Cl}_6$ (Nippon Soda) was converted to $\text{N}_3\text{P}_3\text{F}_6$.⁴ Previously reported procedures were used for preparation of $\text{N}_3\text{P}_3\text{F}_6\text{C}_6\text{CPh}_3$, $\text{N}_3\text{P}_3\text{Cl}_6\text{OCH}=\text{CH}_2$,⁴ and $[\text{CH}(\text{ON}_3\text{P}_3\text{Cl}_6)\text{CH}_2]_n$, (I).⁴ **Measurements.** Gel permeation chromatography was performed on a Waters 202 high pressure liquid chromatograph equipped with 10⁴ and 10⁵ Å microstyragel columns. Thermal analyses were carried out using a Perkin-Elmer TGS-2 thermogravimetric system interfaced with a PETOS thermal analysis data station. Cyclic voltammetry measurements were performed on 0.5mM solutions with Bu_4NPF_6 as supporting electrolyte and SCE reference electrode using a Princeton Applied Research model 273 potentiostat.

Syntheses. Derivatives of $\text{N}_3\text{P}_3\text{Cl}_6\text{OCH}=\text{CH}_2$ were prepared by reactions of stoichiometric amounts of the appropriate nucleophile followed by chromatographic purification. Products of reactions of various nucleophiles with the polymer, $[\text{CH}(\text{ON}_3\text{P}_3\text{Cl}_6)\text{CH}_2]_n$, were isolated by precipitation with methanol except for the methylamino derivative which was isolated by filtration of the precipitated polymer. The reaction of 4-(1-methylethoxy)phenyl lithium⁵ with $\text{N}_3\text{P}_3\text{F}_6\text{C}_6\text{CPh}$ yields 2,4- $\text{N}_3\text{P}_3\text{F}_6\text{C}_6\text{CPh}[(\text{C}_6\text{H}_4\text{C}(\text{CH}_3))_2=\text{CH}_2]$ which undergoes facile copolymerization with styrene using azobis(isobutyronitrile) (AIBN) as an initiator. Reactions of $\text{CO}_2(\text{CO})$ with solutions of this copolymer yields the cobalt carbonyl complex $[\text{CH}(\text{Ph})\text{CH}_2]_n[\text{C}(\text{CH}_3)(\text{N}_3\text{P}_3\text{F}_6\text{C}_6\text{CPh}_3\text{Co}_2(\text{CO}))\text{CH}_2]_n$.

RESULTS AND DISCUSSION

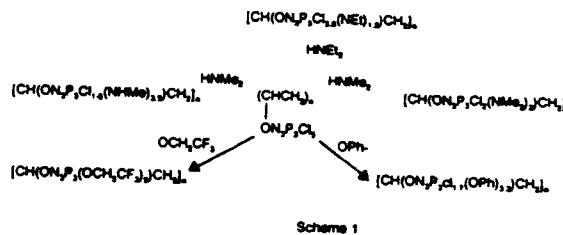
The polymerization of the vinyloxycyclotri-² and tetraphosphazenes leads to highly functionalized polymers with five and seven reactive sites per monomer unit respectively.



Copolymerization of the trimeric and tetrameric derivatives leads to polymers with both six and seven membered rings as substituents. These polymers undergo a remarkable set of thermal decomposition reactions. The first step is a cross linking process wherein the cyclophosphazene serves as the bridging unit between two chains by way of carbon-phosphorus bond formation accompanied by HCl release. The fact that this process occurs at relatively mild conditions suggests the possibility of utilization of the chlorocyclophosphazene unit in thermosetting polymers. The second step, which occurs at much higher temperatures ($> 400^\circ\text{C}$), involves elimination of the oxobridged dimers, $(\text{N}_3\text{P}_3\text{Cl}_6)_2$.

There are two basic routes to chemical modification of the poly(vinyloxyphosphazenes): derivatization of the monomer followed by polymerization or derivatization of the performed polymer. We have previously shown that strongly electron donating substituents will produce vinyloxyphosphazene monomers that do not undergo radical chain homopolymerization.⁷ Since weakly electron donating or electron withdrawing substituents will allow for polymerization, we examined the polymerization of 2,4- $\text{N}_3\text{P}_3\text{Cl}_6(\text{OCH}_2\text{CF}_3)\text{OCH}=\text{CH}_2$, 2,4,6- $\text{N}_3\text{P}_3\text{Cl}_6(\text{OCH}_2\text{CF}_3)_2\text{OCH}=\text{CH}_2$ and $\text{N}_3\text{P}_3(\text{OCH}_2\text{CF}_3)_3\text{OCH}=\text{CH}_2$. In each case, polymerization of the neat liquid monomer (using AIBN as an initiator) proceeded smoothly to give polymers with a broad spectrum of solubility. However, the molecular weights (GPC) in the series $[\text{CH}(\text{ON}_3\text{P}_3\text{Cl}_6(\text{OCH}_2\text{CF}_3)_x)\text{CH}_2]_n$, ($x=1,2,5$) decrease significantly with increasing trifluoroethoxide substitution. This observation indicates chain transfer events involving the trifluoroethoxy substituents and suggests the need to explore the alternative method for producing substituted vinyloxyphosphazene polymers.

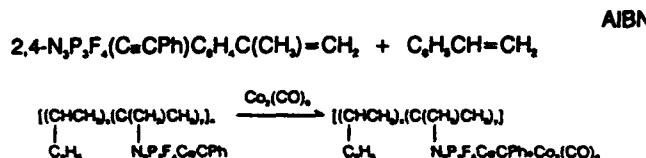
The reactions of I with various nucleophiles has been explored and the synthetic results are summarized in Scheme 1.



Scheme 1

The trifluoroethoxide derivative is a high molecular weight material with all chlorine atoms in the parent polymer (I) being replaced. Thermal decomposition of this polymer follows a simple random scission process while the partially substituted materials undergo the two step process described for I. The reactions of the remaining chlorine atoms in I. This behavior is more like that of the cyclophosphazenes, where reactions are more difficult at high degrees of substitution,¹ than corresponding reactions of poly(dichlorophosphazene).¹ The thermal decomposition behavior also varies in the series of polymers described in Scheme 1. Some follow the two step process seen in I while others produce a much higher char level. In the phenoxy derivative, over 50% of a phosphazene containing (as indicated by IR spectroscopy) char is obtained. A dramatic illustration of simple property modification is seen in the relative solubilities of the methylamino and trifluoroethoxy derivatives where the former is only soluble in water or methanol and the latter is soluble in most solvents with the exception of water and methanol.

Another approach to derivatization of pendant cyclophosphazenes is to work with substituents which can be transformed into more complex units. We have been interested in the reactions of alkyne phosphazenes with organometallic reagents.⁹ As an example of this approach, we have prepared the dicobalt hexacarbonyl derivatives, $N_xP_3F_x[CaCPh_3Co_2(CO)_6]$, ($x=1,2$) and reduced them to radical anions.¹⁰ An analogous polymeric system can be prepared using copolymerization chemistry.¹¹ Reactions of



the copolymer with dicobalt octacarbonyl produces the desired organometallic derivative which undergoes reversible electrochemical reduction to the radical anion.

The studies shown above demonstrate the broad range of reactivity and property modification available via the reactions of polymers with pendant cyclophosphazenes.

ACKNOWLEDGEMENT

This work was supported in part by the Office of Naval Research. The gift of $N_xP_3Cl_x$ from Nippon Soda is appreciated.

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